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## THE COKING OF COAL AT LOW TEMPERATURES

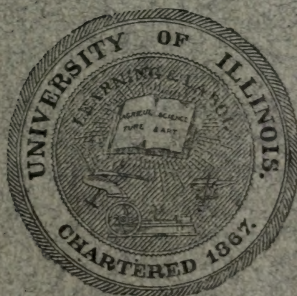
(WITH A PRELIMINARY STUDY OF THE BY-PRODUCTS)

BY

S. W. PARR

AND

H. L. OLIN



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UNIVERSITY OF ILLINOIS  
ENGINEERING EXPERIMENT STATION

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JUNE 1912

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THE COKING OF COAL AT LOW TEMPERATURES

(WITH A PRELIMINARY STUDY OF THE BY-PRODUCTS)

BY S. W. PARR, PROFESSOR OF APPLIED CHEMISTRY, AND H. L. OLIN,  
RESEARCH FELLOW, DEPARTMENT OF CHEMISTRY

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# THE COKING OF COAL AT LOW TEMPERATURES

## I. INTRODUCTION

1. *Purpose of the Investigation.*—The investigations discussed in this bulletin had two general purposes in view: (1) to discover some fundamental facts pertaining to the properties and characteristics of bituminous coals; (2) to determine the feasibility of modifying the composition of raw coal in order that a different type of fuel might be produced, or possibly an alteration accomplished of the entire fuel content into forms better suited to present-day requirements.

2. *Scope of Previous Investigations.*—In earlier experiments<sup>1</sup> (1907-1908), the information developed was mainly of the type indicated under the first division; for example, the experiments early indicated the important role played by small amounts of oxygen in the gases surrounding the heated masses of coal. The ease with which carbonaceous matter absorbed or united with oxygen was so striking that it seemed desirable to follow the matter into detail regarding the temperatures at which oxidation takes place, and its effect upon the material in hand. As a result, the whole matter of coal oxidation at low temperatures was opened up as one of extreme importance. One fundamental fact brought out in the study<sup>2</sup> was the absorbent power of freshly-mined coal for oxygen, and the part oxygen played in producing certain changes in the coal and promoting the initial form of deterioration in storage. Again<sup>3</sup>, the prime element in all the phenomena was seen to be that of oxidation. It will thus be seen that these preliminary studies on low temperature distillation, while mainly bringing into view what might be termed the scientific or fundamental properties of the material, at the same time determined facts which have had much to do with developing the practical application of

<sup>1</sup>The present investigations are a continuation of the work carried on in 1907-8 and presented as a preliminary report under the title of "The Modification of Illinois Coal by Low Temperature Distillation", Bulletin No. 24, University of Illinois, Engineering Experiment Station, by S. W. Parr and C. K. Francis, 1908.

<sup>2</sup>"The Occluded Gases in Coal", Bulletin No. 32, University of Illinois, Engineering Experiment Station, by S. W. Parr and Perry Barker.

<sup>3</sup>"The Weathering of Coal", Bulletin No. 38, University of Illinois, Engineering Experiment Station, by S. W. Parr and W. F. Wheeler; also "The Spontaneous Combustion of Coal", Bulletin No. 46, University of Illinois, Engineering Experiment Station, by S. W. Parr and F. W. Kressmann.

the information in its relation to storage and spontaneous combustion.

In the second phase of the earlier study, i. e., its industrial side as related to the development of a special type of fuel, it seemed to be established that below a certain temperature, say 700° F., the heavy hydrocarbons, those chiefly responsible for the formation of smoke, could be driven off, yielding a gas of high illuminating power, a tar with high percentage of volatile oil, and a solid which, while it could be burned without smoke, was friable and not well adapted to ordinary use as a fuel.

3. *Outline of Present Investigation.*—In the present studies, the friable or non-coking tendency of the earlier product has been found to depend directly upon the amount of oxidation that has occurred both in the preliminary exposure at ordinary temperature and in the process of heating to moderately high temperatures.

The fact that a coke of good texture could be produced when a careful exclusion of oxygen had been effected, has given special interest to the present experiments. In addition, important facts have developed in connection with the study of the various by-products. These by-products have also been more or less modified in their characteristics by the exclusion of oxygen.

Briefly outlined, the present studies have developed three lines of industrial interest.

First: The possibility of developing a smokeless fuel of good texture and admirably suited to domestic as well as to general industrial use where absence of smoke is essential. The accompanying by-products promise to be of special value. These consist of (a) Ammonia, though smaller in quantity than the yield obtained at higher temperatures; (b) Illuminating gas of high candle-power and high heat value; and (c) Tar, which is composed almost entirely of oils, with a minimum amount of pitch and free carbon. Some of the oils produced are of peculiar structure and may have more than passing interest, two of the fractions, for example, being readily oxidizable. The iodine absorption numbers of the lighter fraction are found to be as high as 165.

Second: They suggest a possible method for the manufacture of producer gas which would be free from present difficulties attending the use of bituminous coal, and would convert a



much higher per cent of the fuel into the gaseous form. In view of recent developments in the matter of combustion, efficiencies are possible<sup>1</sup> where gaseous fuel is available which are almost revolutionary in character.

Third: There are opened up interesting possibilities in the production of coke, briquettes or other forms of fuel in a dense and stable form to meet certain requirements of shipping, storing, foundry, and other industrial uses. Certain facts developed in these studies will be found to throw some light on the problem of coking, which is at present but little understood<sup>2</sup>.

It is not intended here to enter into a discussion of these three main topics; they will be taken up again after the details of the experiments have been set forth. The results of the experiments may then with better understanding be made to enter into the conclusions reached.

## II. EXPERIMENTAL WORK

4. *Apparatus.*—The apparatus employed is illustrated in Fig. 1. From the high pressure main at *A*, steam was admitted to *BB*, a  $\frac{5}{8}$ -in. pipe 11 ft. long, fitted with two return elbows. The steam was then heated by a 26-burner combustion furnace, *CC*. The retort *D*, 18 in. by 8 in., containing the coal, was fitted with a head *J* held in place with set-screws and sealed with asbestos. From the retort, the distillates were conducted by a pipe to a condenser *E* connected in turn with a large wash bottle *F*. Here the oils and tars were collected while the gases passed on to the gasometer *G*. A Hoskins nickel-nichrome thermocouple, inserted through a stuffing box *S* and joined to a millivoltmeter *K* measured the temperature of the retort contents. A battery of burners placed directly under the retort provided a means for securing additional heat, which was retained by means of an asbestos-lined oven which entirely surrounded both the retort and the furnace.

5. *Use of Superheated Steam.*—Superheated steam was used in this series of experiments as a medium for carrying the

<sup>1</sup>Surface Combustion. Proc. Am. Gas Inst., 1911. By Prof. W. A. Bone. In this article Prof. Bone gives data showing an efficiency in the generation of steam by use of the principle of surface combustion of 94.2 per cent. It should be noted, however, that this efficiency is based upon the net heating value of gas.

<sup>2</sup>"The question as to what really is the factor that produces the coking tendency characteristic of some coals has been a matter of some speculation among manufacturers and users of coke for two hundred years and we are no nearer to its solution now than were the investigators of two centuries ago."—Iron Age, 1907. F. C. Keighley.

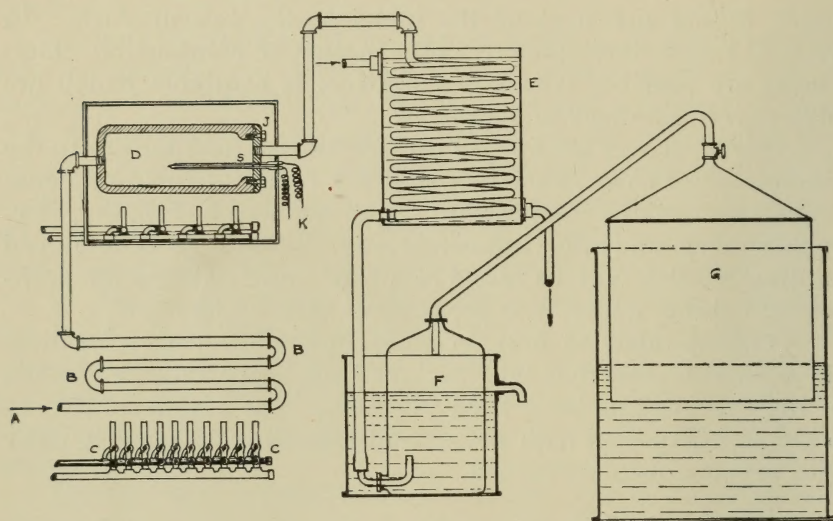


FIG. 1

heat into the coal mass, in order to distribute the heat evenly throughout the coal and thus obviate the necessity for revolving the container. In the earlier experiments (1907-1908), the carbonization was carried on in a cylinder heated externally and mounted on hollow trunions in order to make possible the turning of the receptacle, while at the same time the hollow bearings permitted the admission of various inert gases at one end and the discharge of the distillates at the other. With that device, the frequent turning over of the coal seemed to be unfavorable to the formation of coke having a homogeneous texture. Moreover, the mechanical features were not easily installed. There was positive evidence also of the activity of small quantities of oxygen, which entered by leakage or as an impurity in the circulating gas employed, thereby acting as a disturbing element. There seemed sufficient reasons, therefore, for employing a fixed retort and using superheated steam as the medium for conveying the heat and also for securing a suitable atmosphere for the distillation. As will be seen later under the discussion of the coking of coal, the use of steam in this manner has other advantages which, while not fully appreciated at first, are directly in line with the fundamental conditions upon which depends the property of coke formation.

6. *Coal Used.*—Table 1 gives the data concerning the coals used. It should be noted that since these studies were made for the



purpose of testing the coking powers of the different coals and not to determine their relative commercial values, many of the samples selected were cleaner than the general run-of-mine. The low ash and sulphur percentages result from the exclusion of pyrites.

TABLE 1  
COMPOSITION OF COAL

| Mines<br>Counties—Illinois | Moisture | Ash   | Volatile<br>Matter | Fixed<br>Carbon | Sulphur | B. t. u. |
|----------------------------|----------|-------|--------------------|-----------------|---------|----------|
| Vermilion.....             | 8.80     | 8.72  | 43.05              | 39.43           | 2.88    | 12673    |
| Franklin.....              | 6.84     | 7.38  | 37.96              | 47.82           | 1.33    | 12770    |
| Saline.....                | 3.93     | 5.80  | 37.86              | 52.41           | 1.54    | 13593    |
| Macon.....                 | 8.70     | 12.12 | 39.30              | 40.88           | 2.30    | 11417    |
| Perry.....                 | 7.19     | 10.05 | 35.42              | 47.34           | .80     | 12153    |
| Williamson.....            | 5.30     | 8.55  | 36.50              | 49.65           | 2.77    | 12640    |

7. *Operation.*—A quantity of coal sufficient for one run only from 2500 to 3000 grams, was crushed at one time. In the first experiments, the pieces ranged from  $\frac{1}{4}$  in. to buckwheat size, the dust being removed by a sieve. At first the coal was put directly into the retort, but it was found that the circulation of the steam was retarded, delaying the heating of the mass. To remedy this, a cylindrical sheet-iron container, 6 in. in diameter, perforated with small holes, was made to hold the charge. This shell (see Fig. 2) being smaller than the retort and having a sur-

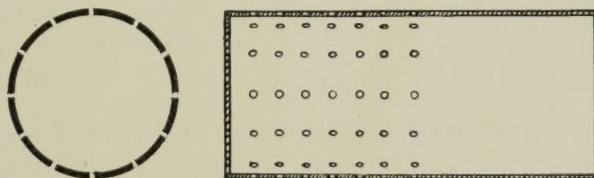


FIG. 2

rounding space of about 1 in., allowed a free distribution of heat. It was used throughout the remaining runs of the series.

Steam was admitted from the main and allowed to blow through the system until the air was entirely displaced. The combustion furnace was next started and then the burners under the retort. The coal was not stirred after heating had begun.

Table 2 exhibits the average working conditions. By improving the facilities for applying external heat to the retort, the time of the later runs was reduced to an average of about five hours.

TABLE 2  
TEST CONDITIONS: FIRST SERIES

| Run No.                                  | 3    | 4     | 5     | 6     | 7     |
|------------------------------------------|------|-------|-------|-------|-------|
| Weight of coal <sup>1</sup> , grams..... | 4800 | 5351  | 2195  | 3498  | 3398  |
| Weight of residue, grams.....            | 4030 | 4112  | 1895  | 2810  | 2895  |
| Max. temp. (degrees C.).....             | 475° | 515°  | 450°  | 410°  | 430°  |
| Ratio of coke.....                       | 84%  | 76.8% | 86.3% | 80.3% | 85.2% |

<sup>1</sup>Nineteen runs were made in the first series, using Williamson Co. coal for the first 10 tests. In the other tests, the coal came from the following counties in the order given, Vermilion, Williamson, Franklin, Saline, Macon, Vermilion, Vermilion, Williamson, Vermilion.

8. *Distribution of Products.*—Table 3 illustrates the distribution of products.

TABLE 3  
EXPERIMENT<sup>2</sup> No. 11

|                                                                                    |                               |
|------------------------------------------------------------------------------------|-------------------------------|
| Coal used <sup>3</sup> .....                                                       | Electric Mine, Danville, Ill. |
| Temperature (average).....                                                         | 450°                          |
| Time of distillation.....                                                          | 5 hr.                         |
| Volatile matter in original coal not including moisture.....                       | 43.00                         |
| Volatile matter in coke residue.....                                               | 27.95                         |
| Volatile matter in coke residue referred to original coal.....                     | 22.01                         |
| Loss in weight of original coal, volatile matter only, not including moisture..... | 20.28                         |
| Total volatile matter derived as above, not including moisture.....                | 42.29                         |
| Total material, removed by distillation including moisture.....                    | 29.10                         |

<sup>2</sup>Selected as a typical example.

<sup>3</sup>For methods of calculating percentages of coal constituents in this and succeeding tables see Bul. No. 16, p. 209, Ill. Geol. Sur.

TABLE 4  
YIELD OF PRODUCTS FOR DIFFERENT PERIODS OF HEATING

| Time of Heating                            | 3 hr.          | 6 hr.          |
|--------------------------------------------|----------------|----------------|
| Coal.....                                  | 3000 grams     | 4000 grams     |
| Coke.....                                  | 2327 grams     | 2902 grams     |
| Per cent coke.....                         | 77.50%         | 72.50%         |
| Weight of tar.....                         | 238.5 grams    | 316.0 grams    |
| Per cent tar.....                          | 7.93%          | 7.90%          |
| Weight of total water.....                 | 208.5 grams    | 348.4 grams    |
| Per cent free moisture.....                | 3.38%          | 3.00%          |
| water constitution.....                    | 3.55% or 6.93% | 5.71% or 8.71% |
| Volume of gas at 760 mm. and 0°.....       | 87 liters      | 154.7 liters   |
| Calculated to cu. ft. per lb. of coal..... | .46 cu. ft.    | .54 cu. ft.    |

From the preceding tables a fair indication is given of the ratio of distribution of the main products of decomposition. A study of these three products, gas, tar and coke, has been made, sufficient to determine their general characteristics and value.



## III. GASES

9. *Analysis of the Gas.*—The methods of Hempel were used in making all gas analyses. For absorbing the illuminants, bromine water checked with the results from fuming sulphuric acid and was free from the disagreeable properties of the latter. The paraffin hydrocarbons were determined by the use of the explosion pipette. Hydrogen was determined separately with palladium sponge, a variation from the ordinary industrial method necessary when higher paraffins are present in the gas. Calorific values were determined with the Parr gas calorimeter.

It is impossible to determine absolutely the paraffin content of a gas by any methods now in general use, when more than two of the homologues of methane are present. However, by measuring the contraction of the gases and the amount of  $\text{CO}_2$  produced in burning them in the explosion pipette, the total volume of the hydrocarbons having the general formula  $\text{C}_n\text{H}_{2n+2}$  may be determined together with the average value for  $n$ . On the assumption that the higher homologues are all ethane, the percentages of methane and ethane may then be computed<sup>1</sup>.

Several analyses of the gases obtained early in the work were made, but on account of air leakage in the gasometer, the results obtained were misleading. Table 5 shows the average of results obtained under satisfactory conditions, from gas evolved at an average temperature of  $400^\circ$ .

TABLE 5  
GAS FROM DANVILLE ELECTRIC MINE COAL

| $\text{H}_2\text{S}$ | $\text{CO}_2$ | Illuminants | $\text{CO}$ | $\text{H}_2$ | $\text{C}_2\text{H}_6$ | $\text{CH}_4$ | $\text{N}_2$ | B. t. u. |
|----------------------|---------------|-------------|-------------|--------------|------------------------|---------------|--------------|----------|
| 3.2                  | 5.7           | 8.3         | 5.2         | 5.0          | 14.4                   | 51.4          | 5.7          | 1032     |

The computed heat value of this gas was 1024 B. t. u. and agrees closely with that determined directly. Heat values of the different gases as given by Abady<sup>2</sup> were used as the basis of calculation.<sup>3</sup>

From the agreement between the observed heat value as shown by the gas calorimeter and the calculated value as derived

<sup>1</sup>Abady, Gas Analyst's Manual, p. 356, 1902.

<sup>2</sup>Gas Analyst's Manual, p. 521, 1902.

<sup>3</sup>According to J. H. Coste (Chemical Engineer, February, 1911) it has been found from Julius Thomsen's figures that the average calorific value of the unsaturated hydrocarbons is equivalent to that of propylene,  $\text{C}_3\text{H}_6$ .

from the constituents, indirect evidence is obtained as to the correctness of the assumption concerning the composition of hydrocarbons assumed to be present in the higher forms.

10. *Heat Value*.—It will be noted that this gas is relatively of high heating value, 1024 B. t. u. per cu. ft. Compared with ordinary city gas at 600 B. t. u. per cu. ft., this gas has a heat value about 70 per cent greater, i. e., 1 cu. ft. at 1024 B. t. u. would be equal to nearly 1.7 cu. ft. at 600 B. t. u.

11. *Sulphuretted Hydrogen*.—The gas is practically free from naphthalene but has a considerable content of  $H_2S$ . The latter feature is unexpected, since the temperature of decomposition of  $FeS_2$  is  $1000^\circ C$ . and above. Doubtless, therefore, the sulphuretted hydrogen present is in the main due to the breaking down of the organic sulphur. It seems to be entirely in the form of  $H_2S$  and, therefore, easily removable by the usual methods of purification. Some of the coke residue from a coal having originally 4 per cent of sulphur was examined to see if any of the iron pyrites,  $FeS_2$ , had been broken down by the temperature employed to ferrous sulphide,  $FeS$ . Five grams were treated with a large excess of dilute hydrochloric acid. The mass was thoroughly washed and the percentage of sulphur remaining determined. Test No. 1 gave 3.55%; No. 2, under identical conditions, 3.70%. A quantity of the same residue kept well moistened was then exposed to air and sunlight for a period of twelve days in order to oxidize any  $FeS$  present to a sulphate. After washing, the sulphur content was 3.74%, indicating that  $FeS$  in the original sample was absent.<sup>1</sup> It is evident, therefore, that the pyritic iron had been little affected by the temperatures of the retort.

12. *Ammonia*.—Any by-product process for the carbonization of coal would, of course, take account of the nitrogen liberated in the form of  $NH_3$ . At the temperature employed in these experiments, it would not be expected that any considerable part of the nitrogen organically present would be decomposed. The following values are shown in a distillation<sup>2</sup> varying in temperature from  $375^\circ$ – $400^\circ C$ . In this work the entire distillate from a run of 3000 grams was retained and the total ammonia of the liquor determined. It was found to contain ammonia as  $NH_3$  sufficient to

<sup>1</sup>On the subject of the decomposition of pyrite, Peters, in *Principles of Copper Smelting*, p. 263, quotes Sticht as saying "At dull red heat  $FeS_2$  loses  $\frac{3}{7}$  of its sulphur and becomes  $FeS$ . At  $1200^\circ$ , it becomes for the first time  $FeS$ ".

<sup>2</sup>Experiments by Mr. E. C. Hull, Fellow in Chemistry, University of Illinois, Engineering Experiment Station, March, 1909.



represent a yield of 0.8 lb. per ton of coal, somewhat less than  $\frac{1}{4}$  of the yield from high temperature distillation. It is not certain that the value of this product would pay for its recovery.

13. *Decomposition of Oxygen Compounds.*—The oxygen compounds upon decomposing form water. They are, therefore, often referred to as the water of constitution. They are properly considered under this division, though not forming permanent gases. It is a question of great interest whether any decomposing action in connection with the temperatures employed has taken place. If such decomposition has occurred, it has by so much enriched the fuel value of the remaining coke for the reason that these compounds are inert and noncombustible and, when present, by so much increase in effect the ash factor so far as combustion is concerned. The fact of their decomposition is shown by the increase of water content in the distillate over and above that which would normally occur from a condensation of the hygroscopic moisture alone. While this fact was not available in the case of distillation with superheated steam, the point was well established in the previous experiments<sup>1</sup>, as also by experiments conducted by Mr. E. C. Hull, not heretofore published, in which careful measurement was kept of the amount of water distillate recovered from the coal used.<sup>2</sup> Thus, from the work of the latter we have the following:

TABLE 6

|                                                                 | 3000 Grams<br>Coal Distilled<br>for 3 hr. Temp.<br>300° to 400° | 4000 Grams<br>Coal Distilled<br>for 6 hr. Temp.<br>300° to 400° |
|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|
| Weight of water in distillate .....                             | 208.5                                                           | 348.4                                                           |
| Weight of free moisture in original coal .....                  | 102.0                                                           | 180.0                                                           |
| Excess water from decomposition of oxygen compound in coal..... | 106.5                                                           | 228.4                                                           |
| Per cent of water from decomposition of oxygen compound .....   | 3.55                                                            | 5.71                                                            |

14. *Summary of Data Concerning the Gaseous Product.*—Distillation of Illinois coals at temperatures averaging 450° C. and not exceeding 500° C. produces a gas having a heating value exceeding 1000 B. t. u. per cu. ft. The yield approximates  $\frac{1}{2}$  cu. ft. per lb. of coal which, at the heat value present, would represent a yield of 1.00 cu. ft. per lb. of a gas with a heat value of 500 B. t. u. per cu. ft. The ammonia yield is low, being approximately 3 lb. of ammonium sulphate per ton of coal. Decom-

<sup>1</sup>Bulletin No. 24. University of Illinois, Engineering Experiment Station. Parr and Francis.

<sup>2</sup>See also Porter and Ovitiz. Bulletin No. 1, U. S. Bureau of Mines, p. 26-28.

position at this temperature extends to the oxygen compounds, which are in the main carried off and appear in the condensate instead of in the gaseous product. This feature will be referred to again under the discussion of the composition and properties of the coke residue.

#### IV. TAR

15. *Composition.*—As already noted, the amount of tar recovered from the distillations approximates  $\frac{1}{2}$  of the yield of volatile matter and in the sample noted where a direct weighing was made (Table 6), this material represents very nearly 8% by weight of the original coal. An exhaustive study of this material would be an elaborate topic for research in itself. We can, therefore, give only the general characteristics of the material as found by fractional distillation as follows:

TABLE 7  
FRACTIONS FROM LOW TEMPERATURE TAR

| Amount of tar (exclusive of water carried over)..... | 375 grams |       |
|------------------------------------------------------|-----------|-------|
| Light oil (20°-100°).....                            | 39.1      | 10.5% |
| Fraction (b) (100°-200°).....                        | 109.1     | 29.1  |
| (c) (200°-240°).....                                 | 111.8     | 29.8  |
| (d) (240°-275°).....                                 | 20.6      | 5.5   |
| Coke residue.....                                    | 80.0      | 21.3  |

From the results as given in Table 7, it will be seen that 75% of the material classed as tar is in reality oils of different specific gravities and thus of much greater value than the pitch proper. This latter product, moreover, is much smaller in amount than is produced with high temperature distillation. In the latter case over one-half of the tar is pitch, with a considerable content of free carbon suspended in the material. The low temperature product is approximately one-fifth a pitch residue with some suspended carbon present, seemingly depending on the extent to which the temperature of the coal mass has been carried above 400°.

16. *Properties of Oils.*—The further examination of the oils distilled from the tar has developed the interesting fact that these oils are readily oxidizable. As a measure of this property the iodine absorption number was determined with results as given in Table 8. It is realized, of course, that the iodine absorption



must include or represent other activities than simple oxidation especially in a complex mixture where members of the aromatic series are present.

TABLE 8

## IODINE ABSORPTION OF OIL DISTILLATE

|                                    |                |
|------------------------------------|----------------|
| Fraction b, 100°-200° (29%).....   | Iodine No. 165 |
| Fraction c, 200°-240° (29.8%)..... | 115-125        |

Further study of the oils recovered is necessary in order to determine their specific values. Their ready oxidizability opens up a very interesting and suggestive field. For example, this feature is a marked characteristic of drying oils, turpentine, etc., used in paint mixtures. The question arises as to whether these oils will have drying qualities, i. e., will they not simply evaporate, leaving no residue, or will they oxidize in such a manner as to produce a film-covering, which will serve as a paint vehicle. Or, in a mixture with a drying oil such as linseed or similar oil, will they promote the peculiar properties of such oils which make them of value for paint mixtures? While only a few general points in this connection have been developed, they indicate characteristics of great interest and, possibly, value. It seems fair to conclude that in some measure at least the iodine absorption numbers are an indication of the avidity of the oils for oxygen. This is shown by the rapid discoloration of the oil when exposed to the air and to the fact that the lighter fraction will yield a dry film on glass at a 45° angle when exposed for 24 hr. under the usual standard requirements for such test. The second fraction has also drying properties, but the process is much slower. Or, rather, a fractionation appears to take place in which the drying oil forms a hard gelatinous film while the non-drying portion segregates into minute globules which are more or less enveloped by the films of oxidized oil. At least, it may be said of the oils which make up the element of the tar, they are available directly as fuel or for enriching or carbureting water gas. For example, if the process were continued to include the manufacture of water gas from the coke residue, the oil of the tar would doubtless enter into the reaction in the same manner as the crude petroleum now used, and thus would furnish the needed enrichment without the clogging effect which results when the attempt is made to use the raw coal directly in the manufacture of water gas.

## V. COKE

17. *Yield of Coke.*—The yield of coke, under average conditions, as already noted in previous tables, is approximately 75% to 80%. This factor will, of course, vary greatly with the amount of ash originally in the coal and on the temperature at which the distillation has been carried on. These items of variation are shown in the following table where material of widely varying composition was used.

TABLE 9  
COMPOSITION OF COKE RESIDUES

|                      | Experiment No. 11<br>Vermilion Co. | Experiment No. 13<br>Franklin Co. | Experiment No. 14<br>Saline Co. |
|----------------------|------------------------------------|-----------------------------------|---------------------------------|
| Moisture.....        | .34                                | .40                               | .28                             |
| Ash.....             | 11.15                              | 9.28                              | 6.97                            |
| Volatile matter..... | 27.61                              | 26.60                             | 23.50                           |
| Fixed Carbon.....    | 59.90                              | 63.72                             | 69.23                           |
| Sulphur.....         | 2.58                               | 1.21                              | 1.20                            |
| B. t. u.....         | 12892                              | 13446                             | 13746                           |

TABLE 10  
SHOWING THE YIELD OF COKE FROM VARIOUS COALS REFERRED TO  
ORIGINAL COAL—DRY BASIS

|                               | Experiment<br>No. 11 | Experiment<br>No. 13 | Experiment<br>No. 14 |
|-------------------------------|----------------------|----------------------|----------------------|
| Ash.....                      | 9.56                 | 7.92                 | 6.04                 |
| Volatile matter expelled..... | 25.48                | 18.00                | 19.12                |
| Residual coke.....            | 78.10                | 84.72                | 84.86                |

18. *Reactions Involved.*—In the transformation illustrated by the change from the composition as given for the raw coal in Table 1 and the residual coke as shown by the table above, No. 9, certain facts may be deduced as follows:

First: there has been, seemingly, a decomposition of the volatile matter in a manner which would increase slightly the factor for fixed carbon. For example, if the fixed carbon be calculated as indicated in Table 11 to a percentage of ash corresponding to that of the raw coal, comparisons will be obtained as follows:

TABLE 11  
COMPARISONS OF FIXED CARBON IN ORIGINAL COALS AND RESIDUES, DRY BASIS

|                                                            | Experiment No. 11<br>Vermilion Co. | Experiment No. 13<br>Franklin Co. | Experiment No. 14<br>Saline Co. |
|------------------------------------------------------------|------------------------------------|-----------------------------------|---------------------------------|
| Fixed carbon in original coal ...                          | 43.24                              | 51.30                             | 54.56                           |
| Fixed carbon in coke residue referred to original ash..... | 46.80                              | 54.10                             | 59.70                           |



19. *Oxygen Removed.*—As has already been stated, the decompositions occurring at temperatures in the neighborhood of 400° C. include the liberation of oxygen, or, as it is frequently designated, the water of constitution. Since this ingredient of the raw coal is non-combustible<sup>1</sup>, it has the same function as so much ash. Its removal, therefore, serves to make of the resulting material a richer or more concentrated fuel. This feature is still further promoted by the removal of the hygroscopic or free moisture which usually exceeds in amount the water of composition. This point may be illustrated by the accompanying table wherein the heat values per pound of the original coal are compared with the heat values per pound of the residual coke. There is also given an estimate of the amount of non-combustible material removed in the form of water in the process of decomposition.

TABLE 12

| Samples             | B. t. u. per<br>lb. As<br>Received | B. t. u.<br>After<br>Treatment<br>per lb. | Gain<br>Thermal<br>Units | Gain<br>per cent | Estimated<br>Loss of Total<br>Non-combustible Free and<br>Combined<br>Moisture |
|---------------------|------------------------------------|-------------------------------------------|--------------------------|------------------|--------------------------------------------------------------------------------|
| Williamson Co. .... | 12695                              | 13150                                     | 455                      | 3.60             | 10.30                                                                          |
| Saline Co. ....     | 13583                              | 13746                                     | 163                      | 1.63             | 8.93                                                                           |
| Vermilion Co. ....  | 12673                              | 12892                                     | 219                      | 1.72             | 13.30                                                                          |

20. *Properties, Porosity, Hardness, etc.*—The coke material obtained by this process varies in character somewhat with the kind of coal used, and also the amount of pressure employed during the carbonization. The Williamson Co. coal, for example, gives a coke of much finer texture and less porosity than the coal from Vermilion Co. With a view to determining the reason for this greater porosity or to finding the conditions that would modify it, the attempt was made to carry on a test with the coal sample under pressure. To this end the following apparatus was used:

21. *Apparatus.*—A, Fig. 3, is an iron cylinder, 8 in. by 4 in., fitted with screw caps B and B<sup>1</sup>, which received the coal. The movable piston C to which is attached a long rod D, is pressed against the charge by tightening the nuts EE. The cylinder is perforated with small holes to allow the escape of gases. This contrivance was fitted into the retort originally used and heat was applied as before.

<sup>1</sup>Bulletin No. 3, Illinois Geological Survey, p. 32-33.

Exhibit 1 shows the results obtained when pressure is applied slowly during the entire heating period. The outer portions passing through the temporary state of fusion soon harden and form a wall which resists external pressure. The inner core, therefore, is extremely porous. When sufficient pres-

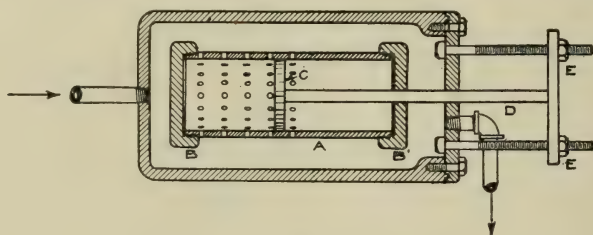


FIG. 3

sure is applied, the outer part fractures and, as in this case, the residue comes out broken up into small pieces. The coke shown in the figure is from coal from Perry Co. The specific gravity of the outer portions of the mass is .733 against .652 when coked without pressure.

It was evident, therefore, that in order to get a firm block, pressure must be constant. In the next run, the charge was rammed into the cylinder and the piston was screwed up tightly but not moved after heating had begun. The resulting column cohered well and showed the same increase in specific gravity as the one mentioned above.

22. *Illustrations of Various Products.*—An interesting feature of the product is the complete fusion of the mass, where proper conditions exist, i. e., the individual particles of coal of buck-wheat or pea size have completely lost their identity, the resulting homogeneous mass showing no lines of demarcation from the original pieces of coal. The texture, however, in some cases is finer or closer than in others. These points are well illustrated in photographs of typical masses as reproduced in exhibits 2 and 3, for coals from southern Illinois. Exhibit 4 represents a somewhat coarser texture. It was made from Vermilion Co. coal. For the composition of these samples, reference is made to Table 9, p. 14. Exhibit 2 from Saline Co. coal showed a crushing strength of 750 lb. per sq. in.<sup>1</sup>; exhibit 3 from a Franklin

<sup>1</sup>John Fulton, (*Coke*, p. 334.) gives 1200 lb. per sq. in. as the ultimate crushing strength of standard Connellsville coke; by-product coke is, in general, considerably stronger.

The crushing strength is important in reference to the load or burden the coke can withstand in the furnace without crushing.



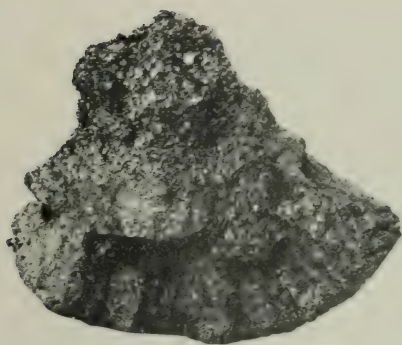


Exhibit 1

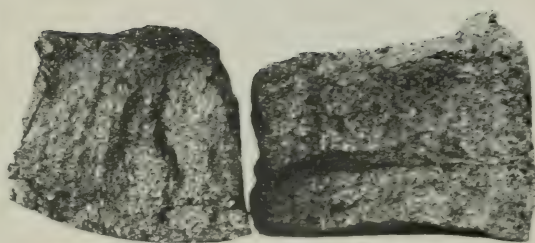


Exhibit 2

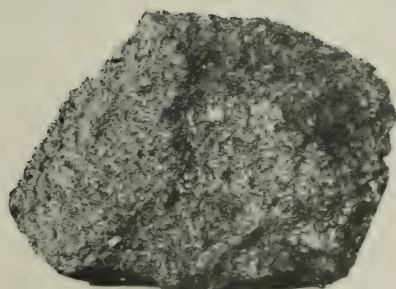


Exhibit 3

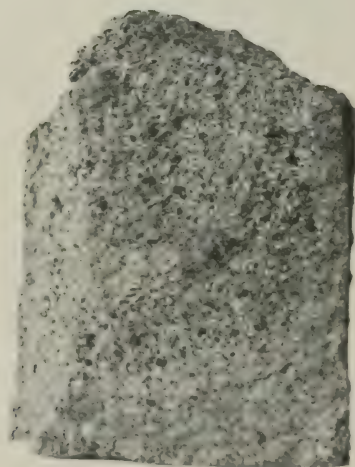


Exhibit 4



Exhibit 5

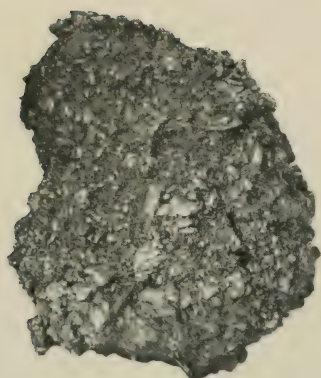


Exhibit 6

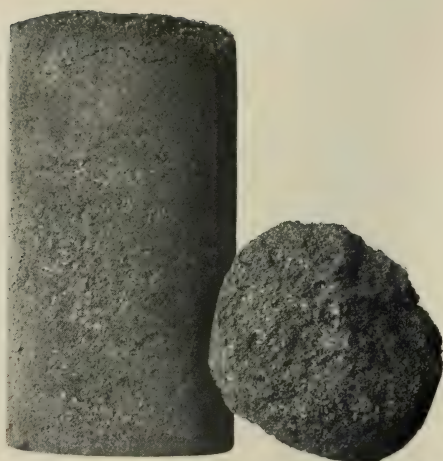


Exhibit 7

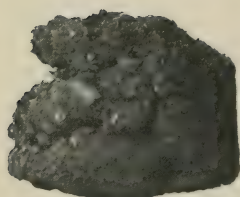


Exhibit 8

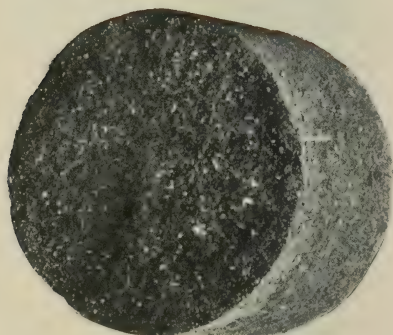


Exhibit 9

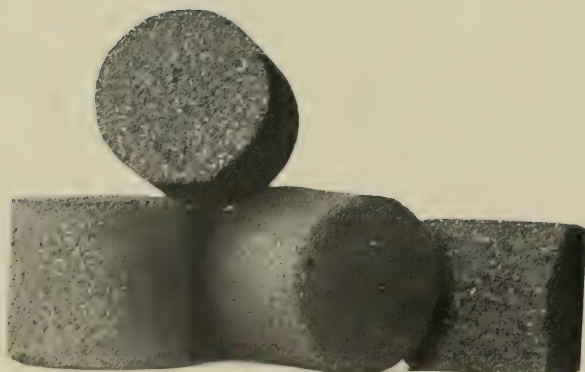


Exhibit 10



Co. sample crushed at 900 lb. On account of its coarse cellular structure, exhibit 4 showed little rigidity, and broke down at a pressure of 300 lb.

23. *Resume Relating to the Coke Product.*—It is evident upon examination of the coke product obtained, as above described, that we have here a fuel of firm texture, not readily broken down by handling and producible in the most convenient sizes for handling and for efficiency in combustion. It is, moreover, in a more concentrated form, in that for the most part, the free moisture and the water of constitution have both been removed. Thus in freshly mined coal there would be eliminated from 15 to 20 per cent of inactive material. Again, the heavy hydrocarbons have been removed. These are the constituents most directly responsible for the formation of smoke in the combustion of untreated coal. It is to be noted further that because this coke has been subjected to a temperature just approaching a red heat, it will not begin to evolve volatile matter, when thrown upon the fire, before it again comes up to or passes that temperature.

The effect of this point is twofold: first, there is obviated the cooling effect which must be necessary in the vaporization of moisture in the raw coal which also lowers the temperature just when a high temperature is needed for burning the heavy hydrocarbons; and second, the remaining gases to be evolved consist almost wholly of ethane or marsh gas ( $\text{CH}_4$ ) and hydrogen, both of which are readily combustible. The hydrogen, of course, burns with a non-luminous flame and is incapable of making smoke. The marsh gas ( $\text{CH}_4$ ), though it has carbon in its composition, adds but little luminosity to the flame and is almost incapable of producing smoke in the process of combustion.

It may be well to analyze briefly the processes of combustion as they occur in an ordinary hand-fired furnace. The first result of throwing a mass of coal upon a fire is to lower the temperature during the time of volatilization of the moisture in the coal. Theoretically, the temperature of the mass during this process would remain at or slightly below  $100^\circ \text{C}$ .

Other factors tending to lower the temperature would be the specific heat<sup>1</sup> of the coal and the heat necessary to effect the decomposition, since it is probable that the decomposition reactions are endothermic up to approximately  $300^\circ \text{C}$ .

<sup>1</sup>Bulletin No. 46, University of Illinois Engineering Experiment Station, Parr and Kressman, p. 34.

<sup>2</sup>Bulletin No. 24, University of Illinois, Engineering Experiment Station, Parr and Francis, p. 46-47.

It is to be noted that during this depression of the general temperature there is being distilled from the coal such volatile substances as are liberated at these lower temperatures. This point can best be illustrated by means of the accompanying diagram. In Fig. 4, the region between the lines A and B may be assumed to include those volatile constituents that are driven off at a temperature below  $400^{\circ}\text{C}$ . This area includes the free moisture of the coal, the combined moisture or water of constitution, or as some prefer, the oxygen compounds of the coal, shown on the chart as inert volatile; and, in addition, some of the pure hydrocarbons which constitute a portion of the true volatile combustible matter. It is, moreover, the nature of this latter or volatile combustible material with which we are just now concerned in this discussion of the processes of combustion. It is to be noted first that this volatile matter contains the

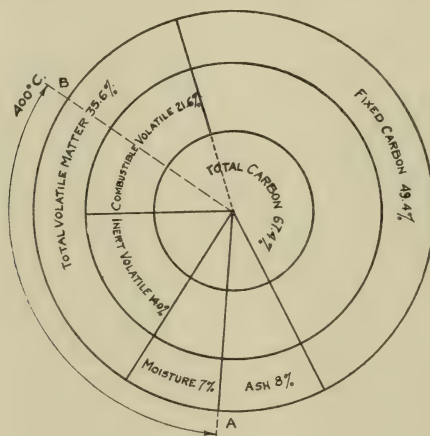


FIG. 4

bulk of the heavy hydrocarbons. By this is meant that they belong to the higher series of any of the homologous compounds present which in general are characterized by a higher percentage of carbon. For example, if the series is that of marsh gas or methane  $\text{CH}_4$ , i. e.,  $\text{C}_n\text{H}_{2n+2}$ , then the next higher order of this series would be ethane or  $\text{C}_2\text{H}_6$ , and the next, propane or  $\text{C}_3\text{H}_8$ . The carbon percentages, respectively, being 75, 80, 81.8, etc. Again a very considerable part of the volatile matter delivered at this temperature belongs to the methylene series  $\text{C}_n\text{H}_{2n}$ , and the first known member of the series is ethylene or olefiant gas,  $\text{C}_2\text{H}_4$ , with a carbon percentage of 92.92. Moreover,



this last compound may be made to break down under higher heat into members of other series, as acetylene,  $C_4H_2$ , benzene,  $C_6H_6$ , and naphthalene,  $C_{10}H_8$ . Other members of the ethylene or paraffin series are found which ally the resulting complex mixture quite closely to the very complicated compounds with which we are familiar in petroleum.

The point to be noted in this phase of the discussion is the fact that these compounds discharged at this relatively low temperature, and having these high percentages of carbon, are the most difficult of complete combustion without the formation of smoke.

It is not necessary here to discuss the mechanics of combustion of hydrocarbons. As a result of the researches of H. B. Dixon<sup>1</sup> and of Professor Bone<sup>2</sup> the selective theory of oxygen for hydrogen or the dogma of "preferential combustion of hydrogen" has been obliged to give place to the theory of the intermediate formation of "oxygenated" or "hydroxylated" molecules. In any event, or whatever the theory finally developed by Professor Bone in his most important researches on combustion, the fact remains that these heavier hydrocarbons are the most difficult of all with which to effect complete combustion, and that even under favorable circumstances the tendency in their combustion is to form condensation products in which free carbon largely predominates. The faulty reaction is thereby made visible to the eye as smoke. A good illustration of this fact is found in acetylene gas, which requires a special burner with special provision for an extra oxygen supply in order to produce a smokeless flame.

Smokeless combustion of raw coal is secured, therefore, by observing the principles indicated above; i. e., there must be uniform and gradual accession of fresh coal and a combustion chamber maintained at a sufficiently high temperature, and the same extending over a sufficient space to permit of ultimate mixing and contact of the oxygen with the combustible gases. Other conditions such as accelerating the reaction by introducing the principle of surface combustion, as developed by Professor Bone, may at some time be added to the mechanical and physical conditions now in vogue. But while these provisions are readily adapted to large steam generating units, they are impossible of application to the larger members of combus-

<sup>1</sup>Phil. Trans. 1893, 159; Trans. Chem. Soc. 61, 873 (1892);

<sup>2</sup>Chem. News, 102, 309 (1911).

tion processes such as are common to the small plant, house heaters, and possibly to locomotives. It is these latter cases especially that demand a modified fuel which can be burned without the formation of smoke.

It will thus be seen that in the low temperature distillation of coal, processes have been put into operation which have taken out the heavy smoke-producing ingredients, and have also removed the moisture, both free and combined, which are chiefly responsible for the depression of temperatures under ordinary conditions. There is left, moreover, as volatile matter, practically these volatile substances only; methane  $\text{CH}_4$  and hydrogen, which most easily of all the gaseous products from coal, maintain a smokeless combustion.

## VI. THE FORMATION OF COKE

The experiments as thus far conducted seem to throw some light upon the matter of coke formation. In this discussion of the theories involved, it may be helpful to formulate certain hypothetical conditions which have had more or less confirmation in these studies, as follows:

First: For the formation of coke there must be present certain bodies which have a rather definite melting point.

Second: The temperature at which decomposition takes place must be above the melting point.

Third: Where the compounds that satisfy the first and second conditions are unsaturated, it is possible by subjecting them to oxidation to so lower the temperature of decomposition as to alter the second condition prescribed, in which case coking will not occur.

*Discussion of Conditions.*—The first condition prescribed above may be well illustrated by the behavior of sucrose or cane sugar. This substance has a rather low melting point, say,  $160^{\circ}\text{C}$ . This melting point, however, is just below the temperature of decomposition. Where this point is reached, gaseous products in the form of steam, etc., are delivered, leaving behind, if the high temperature is continued, a mass of coke. On the other hand, if starch is heated in a similar manner, it does not melt but its first action is that of decomposition. When this is carried to completion, there remains not a strongly coherent mass but easily disintegrated particles of carbon. Pure cellulose behaves in a still more striking manner, showing no fusion properties whatever as may be demonstrated by distilling in a closed



tube some cotton fiber, or other form of cellulose such as filter paper beaten to a pulp and dried. Wood, however, if not disintegrated, as in the form of sawdust, has enough resinous material closely associated with the fibrous structure to bind the carbon filaments resulting from the decomposition of the cellulose by reason of the fact that these gums, or resins, have a melting point below that of their decomposition temperatures, and thus form a binding film of carbon throughout the mass, producing a sort of coking effect which we find in charcoal.

In the case of Illinois coals, we find the first prerequisite formulated above, as present in a marked degree. As an illustration of the fact of a low melting point, reference is made to exhibit 5, which is a photograph of a mass of such material, which exuded from a sample of Vermilion Co. coal, subjected to the usual treatment as described on p. 7. The lump shown is a part of a mass that flowed out of the container, forming a bubble-like puddle. It would seem, therefore, that this type of coal from the north Danville field (Electric mine) has the first essential for coke formation in a marked degree.

As illustrating the conditions which exist where oxidation had been allowed to take place, an example is given in exhibit 6. This was made from a weathered sample of coal from Niantic. It had little if any tendency to fuse; the individual particles of coal still retain their form and the mass may be easily crumbled between the fingers. It should be noted that this result is not due to any inherent quality possessed by the original coal; a Danville mine sample, for instance, weathered to a like degree, gives the same results.

*Test No. 9.*—Another verification of this point, though in a more marked manner, was the result of test No. 9. The coal used was the fine material which had collected from the preparation of the previous tests, all of which had given excellent samples of coke in their freshly prepared condition. A quantity of coal passing through a 40-mesh sieve had accumulated through a period of about six weeks and had been stored in an ordinary coal hod in the grinding room. After being heated for eleven hours under conditions identical with those of the preceding runs, it showed no signs of fusion and was entirely without coking properties.

It is evident from these tests that the very great avidity of fresh coal for oxygen is evidence of the presence of those compounds which satisfy the first of the hypothetical conditions,

p. 17. and the subjection of the coal to oxidation destroys the fusion property of the fresh coal and produces a condition corresponding to that described under the third proposition, in which the coking property is lost.

Other studies on the nature of the coking process were carried out as follows: The apparent plasticity exhibited by the coal during certain stages of the treatment suggested the idea of compressing it into a briquette at the time when it would most easily yield to pressure and when it would presumably cohere without requiring an artificial binder. Accordingly, a cupel press with a pressure of 500 lb. was provided and the retort was charged with Danville mine coal. At the time of maximum evolution of gas, the heat was suddenly shut off and the retort quickly opened. It was found at this point that the outer and hotter portion of the mass was hard and unyielding. A soft inner core was discovered, however, and portions of this were put into the press. The resulting briquette is shown in exhibit 8. The escaping gases have swollen it considerably. Determinations of the amount of volatile matter possessed by the coal when in the plastic condition showed that this constituent had been reduced very little,—from 38 % to 30 %. In short, the state of fusion seems to exist in early stages of distillation but disappears before the process has proceeded far.

In one of the earlier tests with Danville mine coal using the apparatus described in Fig. 3, the extreme fusibility of this type was again demonstrated. As the piston was slowly forced in, pencils of bituminous matter were squeezed out through the holes of the cylinder. Exhibit 5 includes some of these nodules. The fact that there was a selective separation of bitumen is proved by a comparison of the ash values, the residue as a whole having 13 %, the nodules, 8 % of ash.

The readiness with which the cementing material ran to waste seemed to indicate that the coal contained a superfluous amount of it—more than was necessary for binding itself together. The correctness of this view was shown by a series of runs in which crushed gas house coke and anthracite were heated with varying amounts of bituminous coal.

Exhibit 7 shows the hard firm product resulting from the mixture of equal parts of Majestic bituminous coal and gas house coke, both crushed to 20 mesh. Fairly good results were obtained in the next run with 75 % of the coke and only 25 % of Danville Electric coal. In like manner, powdered an-



thracite and bituminous coal in ratios varying from 1 : 1 to 3 : 1 were firmly cemented together. Pitchy material no longer exuded from the retort, being absorbed, seemingly, by the added substance.

One of the essential factors in this scheme for briquetting loose infusible material with bituminous coal is the use of the press for keeping the two substances in close contact. On account of the difficulty of applying such a contrivance in industrial work, attempts were made to attain the desired end by using temporary binders, i. e., substances which might hold the particles together closely until the permanent coal binder could relieve them.

Mixtures of Danville mine coal and Danville mine coke residue No. 17 in the proportion 3 : 1 were thoroughly moistened with water and pressed (1) in the cupel machine and (2) in a testing machine up to 1000 lb. per sq. in. Neither of the briquettes survived the subsequent heating, being disintegrated, seemingly, by the escaping steam. The same effect, though to a much less degree, was noted when coal tar was employed. The resulting briquette retained its shape, but was rather soft and friable. Crude molasses, of all the binding materials tried, proved to be the best for this purpose. Different percentages of the molasses, ranging from 5 to 15, were tested out at different times. Below ten per cent the strength of the briquette was much diminished. Exhibit 9 is a 3:1 mixture of Danville mine coke residue and fresh Danville mine coal, both ground to 20 mesh, first bound with 11 % of molasses and then pressed in the cupel machine. The cake was next heated in the retort under the atmospheric conditions of all the preceding runs. This briquette 2 in. high and 2 in. in diameter, has a crushing strength of 550 lb. per sq. in. Exhibit 10 shows anthracite briquettes made in the same way. They have a specific gravity of 1.02 and crush at 650 lb. per sq. in.

These tests seem to show that the fusible substance of Illinois coals is the true binding material in the coking process; that it is present in such abundance as to produce a coke of too open and spongy a character as a result of the evolution of the large amount of gaseous products which result from its decomposition. In this respect, it is paralleled by the behavior of sugar in the process of coking, which yields as a result of the large volume of escaping gases a very porous mass of sugar, coke or carbon. However, if the raw coal is mixed with a considerable

amount of material which has already gone through the coking process, or which has at least given off the larger part of its gases, and then has been reduced to a fine division like breeze, the cementing material of the fresh coal is able to disseminate throughout the mass, and the gases may also escape without blowing it into a spongy mass, with the result that a coke of good texture is formed. Exactly in a similar way, if molasses or other sucrose or glucose material be substituted for the fresh coal, we shall have again the formation of a dense coke capable of retaining its shape under conditions of firing much better than where a plastic binder is used. In both cases a strongly cohering mass is produced which meets the requirements of handling, storage, and combustion with the greatest efficiency and the least formation of smoke. A small admixture of raw coal may thus be made to serve the purpose of a binder for material otherwise wasted as coke breeze at a cost which would enable it to compete with the pitch binders now in use. It also suggests a process of fractional coking, or coking in two stages. The first result at the lower temperature furnishes a product which, when ground to a moderate degree of fineness and mixed with a small portion of fresh raw coal, would furnish the essential conditions for producing a coke of dense nature with a binder so distributed as to give the material a strength quite comparable with that produced by coals of the regular coking variety. Moreover, an advantage would be evident in such material, especially for use in household appliances, in that it would be more lively in combustion and less difficult of manipulation in the matter of maintaining a fire than coke made by the usual methods.

One point further is to be noted in this connection. It was said at the beginning of the discussion that superheated steam was employed for the purpose of conveying heat into the material so that it would not be necessary to revolve the apparatus in order to secure an even distribution of heat. It is seen from the above detail of the essential conditions to be observed in the coking of coals, at least of this class, that an atmosphere free from oxygen is of prime importance. Indeed following the indicated requirement, the coal should be fresh, or as recently mined as possible, and in any event retained in larger sizes than in a broken down or a fine state of division, in order that the least possible opportunity be given for the absorption of oxygen. Furthermore, by first admitting steam or bringing the coal into an atmosphere of



superheated steam, the effect is to drive out such oxygen as has been occluded or absorbed by the coal and as yet not chemically combined. This is also brought about at temperatures and other conditions least conducive to a reaction between oxygen and the coal substance. Moreover, from former experiments,<sup>1</sup> it has been shown that no reaction at these temperatures takes place between the steam itself and the coal. These principles have an important bearing on certain recent tendencies to concentrate gas production and coke manufacture in large units and distribute the gaseous products at high pressure. From the above, it would seem that the nearer such units were located to the mine or pit-mouth, the better. If it is found, as seems probable, that the coke residue is a suitable material for further continuation of the gas-making process for the manufacture of producer gas, then the above advantages and essential conditions would be magnified.

A discussion<sup>2</sup> by Prof. Lewes, relating to English coals, bears such a striking resemblance to the facts developed in our own work on Illinois coals that the references have especial interest in this connection. Lewes develops his theories on the basis of the existence in coals of four types of degradation products which have all come from two original forms of vegetation: viz: cellulose or lignose, and resinous bodies such as the spores of the lycopodia. The first form of vegetation, i. e., the cellulose, has produced the coal compounds of the humic and ulmic types, while the resinous bodies have produced the other three, viz: (1) resinous bodies with but little alteration; (2) isometric or other slight modifications in form rather than of composition; and (3) decomposition products from resins produced by the action of heat and pressure and consisting of a long series of both saturated and unsaturated compounds, hydrocarbons of the hydro-aromatic series, and saturated hydrocarbons, like hexane, pentane, etc.

"All these degradation products of the original vegetation are to be found in the bituminous coals, the residual body and humus forming the basis, which is luted together by the hydrocarbons and resins, and the characteristics of the various kinds of coal are dependent upon the proportions in which the four groups of the conglomerate are present. \* \* \* The resin bodies and hydrocarbons which form the cementing portion in the coal melt between 300° and 320° C. and if a coarsely powdered sample of the coal becomes pasty or semi-fluid at this temperature,

<sup>1</sup> Parr and Francis, p. 45, Bulletin No. 24, Engineering Experiment Station.

<sup>2</sup> A recent contribution to the theories of coke formation is made in a lecture by Vivian B. Lewes, Professor of Chemistry, Royal Naval College, Greenwich, England, published in *Progressive Age*, Dec. 15, 1911, page 1030.

it is a strong inference that the coal will coke on carbonization, a fact noted by Anderson, and which I have found very useful in practice as a rough test. About these temperatures also the resin bodies and hydrocarbons begin to decompose.

The resin bodies at low temperature yield saturated hydrocarbons, unsaturated, chiefly hexahydrides or naphthenes, together with some oxygenated compounds, while the hydrocarbons yield paraffins and liquid products, all these primary constituents undergoing further decompositions at slightly higher temperatures. The liquids so produced begin to distill out as tar vapors and hydrocarbon gases, and leave behind with the residuum pitch, which at 500°C forms a mass already well coked together if the residuum from the humus is not too large in quantity; the coke formed at this temperature is, however, soft, but if the heat be now raised to 1000°C, the pitch residue undergoes further decomposition, yielding gas and leaving carbon, which binds the mass into a hard coke."

He discusses further the action of oxygen upon certain of the initial constituents, referring to the investigations of Boudouard.

"Boudouard has shown that when coal is weathered humus bodies are produced and the coking power lessened or destroyed. In seven samples of various coals the humus constituents were increased by the oxidation, which seems to show that the action of the absorbed oxygen is to attack the resin compounds, and as we know that carbon dioxide and moisture are the chief products of the earlier stages of heating of masses of coal, it seems probable that the result is a conversion of resinic into humus bodies with evolution of these gases, and it is this change which leads to the serious deterioration in the gas and tar made coal which has been too long in store, while the fact that a cannel coal like Boghead or a shale do not weather is partly due to their dense structure and also is an indication that the resin bodies of which they are chiefly composed are of a different type, a fact borne out by their resistance to certain coal solvents which freely attack the ordinary resin matter."

A continuation of studies along this line is being made. Mention has been made concerning the adaptability of the coke thus produced to use in suction gas producers for furnishing fuel to gas engines. Its freedom from tar, oils, and the heavier products of distillation, which clog and render impossible the use of raw bituminous coals of this type, would seem to offer a solution of these fundamental difficulties. Further studies along this line are also being made.

## VII. SUMMARY AND CONCLUSIONS

1. Coals of the Illinois type can be coked at a temperature approximately 400° or 450° C.

2. The gaseous products consist chiefly of illuminants of high candle-power, and represent, together with the condensible



material under (3) following, the chief elements involved in formation of smoke in the ordinary combustion of raw coal. The nitrogen of the coal is liberated as  $\text{NH}_3$ , at these temperatures, in amounts representing approximately 20% of the total nitrogen present.

3. The condensible distillate consists largely of oils with the minimum amount of tar and free carbon. The oils represent positive values for fuel, for carburetting water gas, or for other specific uses on account of their chemical characteristics as unsaturated compounds.

4. The coke residue has special characteristics which seem to make it of value as a concentrated fuel, capable of combustion without the formation of smoke, suitable for storing without the possibility of spontaneous combustion, and presumably adapted to the manufacture of gas for use in the suction gas producer.

5. Certain facts seem to have been developed concerning the principles involved in the formation of coke which may open the way to the production of a kind of coke of such texture and strength as to make it acceptable for uses that are not now possible with coke made from similar coal, but formed under ordinary conditions, such as are found in the ordinary gas-house retort practice, or that of the by-product coke-oven.

Other considerations<sup>1</sup> are pertinent in this connection, such as losses and pollution of the atmosphere which accompany the production of smoke<sup>2</sup>.

<sup>1</sup>As illustrating the present-day appreciation of matters connected with fuel economy and activity of thought concerning remedial measures, a quotation is here made from the presidential address of Sir William Ramsey before the British Association for the Advancement of Science at York, Eng., July, 1911. (Science, Vol. 34, p. 302, Sept., 1911.)

"The domestic fire problem is also one which claims our instant attention. It is best grappled with from the point of view of smoke. Although the actual thermal loss of energy in the form of smoke is small, still the presence of smoke is a sign of waste of fuel and careless stoking. In works, mechanical stokers, which insure regularity in firing and complete combustion of fuel are more and more widely replacing hand-firing. But we are still utterly wasteful in our consumption of fuel in domestic fires. These considerations would point to the conversion at the pit-mouth of the energy, using as intermediary, turbines or preferably, gas-engines; and distributing the electrical energy to where it is wanted. The use of gas engines may, if desired, be accompanied by the production of half-distilled coal, a fuel which burns nearly without smoke, and one which is suitable for domestic fires.

<sup>2</sup>It is not necessary to multiply arguments for the prevention of smoke. However, a recent article in the Journal of the Society of Chemical Industry, December 15, 1911, by Prof. J. B. Cohen and A. G. Ruston, contains some very striking facts developed in their study of the smoke problem. A few extracts may be given as follows:

"The average per cent of soot passing up the chimney, in 12 analyses including eight of Yorkshire coals, two of Durham coals, and two of Wigan coals, amounted to 6.5 per cent on the carbon burnt. This quantity 6.5 per cent seems a very high figure, representing an annual loss of nearly two million tons on the estimated domestic consumption of 32 million tons. The average deposit of soot over the whole of Leeds will therefore correspond to at least 220 tons per square mile per annum. The tar contained in the soot adheres so tenaciously to everything that it is not easily removed by the rain. The leaves of trees and evergreens in particular get coated with this black deposit. Unfortunately, it does more than blacken the vegetation; it covers the whole leaf over with a kind of varnish, and fills up the pores or stomata, thus checking the natural process of transpiration and assimilation. It is in fact no uncommon thing to find in the case of leaves of conifers grown in Leeds that 80 per cent of the stomata are choked up with tar."

Further studies have in mind the carrying out of the processes as indicated with apparatus involving the continuous feature, subjecting the mass at the point of greatest fusibility to the pressure of the oncoming material and producing the coke in amount sufficient for testing its properties in the gas producer and for combustion in other ways which would test its properties as a smokeless fuel.



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## APPENDIX

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## APPENDIX

## I. INTRODUCTION.

HISTORICAL<sup>1</sup>

## STUDIES IN THE LOW TEMPERATURE DISTILLATION OF COAL.

Researches in the low temperature distillation of bituminous coals have been carried on at the University of Illinois since 1902<sup>2</sup>. In a series of preliminary experiments, on heating coal to temperatures ranging from 250° to 500° for periods of less than an hour, it was found that the percentage of fixed carbon was increased by more than 25% and that there was a corresponding decrease in volatile matter to a point where the formation of smoke was prevented altogether.

In order to eliminate as far as possible those variables which would result from oxidation, Parr and Francis in continuing this work heated Illinois coals in non-oxidizing atmospheres. Choosing nitrogen first as the most suitable medium for this purpose, a careful study was made of the quantity and composition of the gases and heavy residues produced at different temperatures below 400° C. With a view to securing an absolutely inert atmosphere, after finding that the ordinary commercial nitrogen was contaminated with oxygen, the air in the retort was displaced by steam.

The coals heated in these media underwent changes which rendered them smokeless in ordinary combustion. However, on account of the rotary motion given the retort in order to equalize the temperatures, the coke product came out in a loose granular state much like that of the original coal.

In the course of some of the experiments, while using oxygen as the atmospheric medium, rises in the thermometer readings were observed at unexpectedly low temperatures, seemingly independent of the amount of external heat supplied. This suggested the idea of a second series of tests entirely separate from the first, to determine the temperatures at which oxidation begins. The method of procedure was to allow the retort to cool slowly

<sup>1</sup>In assembling the literature relating to the carbonization of coal, it has been planned to bring together first, all of the references to low temperature distillation including the studies of the by-products, followed by references to the theories concerning coke formation and the carbonization of coal in general.

<sup>2</sup>Ill. Geol. Surv., Bull. No. 4, by S. W. Parr, p. 97, 1906.



until a drop of say  $50^{\circ}$  had been recorded. Oxygen was then admitted and the resulting temperature was noted. A rise was considered proof of oxidation. This was repeated until a point was reached where no rise in temperature occurred on the readmission of oxygen. In this way it was found that pulverized bituminous coals in pure oxygen began to oxidize at about  $125^{\circ}$  and that they ignited at about  $460^{\circ}$ . With diluted oxygen the temperatures were somewhat higher.

While making some of their tests with atmospheres of steam it was observed that near the temperature of  $315^{\circ}$  the mercury made an abrupt rise incommensurate with the amount of external heat added. After allowing the coal to cool to  $300^{\circ}$  and then again heating up to  $315^{\circ}$  the same phenomenon was observed. No appearance of carbon dioxide accompanied this sudden rise. A tentative explanation is that it was due to the exothermic character of decompositions occurring at that stage.

In considering the subject of oxidation temperatures,<sup>1</sup> it was found that freshly-mined coal immediately begins to exude hydrocarbons and to absorb oxygen and that it retains its avidity for oxygen for an indefinite length of time. The exact result of this absorption was not fully determined, but it seems probable that under favorable temperature conditions it would tend to hasten combustion.

Constam and Schlapfer<sup>2</sup> publishing "Studies in the Gasifying of the Principal Types of Coal" report that the percentage of oxides of carbon included in the gases given off in distilling coal varies with the oxygen content of the coal itself.

R. T. Chamberlain<sup>3</sup>, studying the causes of mine dust explosions, found that fresh coal absorbs a large quantity of oxygen but that even under a vacuum it gives off very little. He determined further that coal bottled in air for several weeks yields some carbon dioxide but an amount equivalent to only a small part of the oxygen absorbed. This he thought, might be due to the presence of unsaturated compounds in the coal, which form addition products with oxygen.

Mahler and Charion<sup>4</sup> found that when dry air was passed over pulverized coal at temperatures below  $100^{\circ}$ , measurable quantities of water, carbon dioxide and carbon monoxide were

<sup>1</sup>Bulletin No. 32, By Parr and Barker, Engineering Experiment Station, University of Illinois. (1910).

<sup>2</sup>Jour. Gasbel. 49, 741, 774. (1906).

<sup>3</sup>Bulletin No. 383, U. S. Geol. Sur. (1909).

<sup>4</sup>Compt. rend. 150, 1521, 1604. (1910).

given off. Between  $125^{\circ}$  and  $200^{\circ}$  the liberation of water was so greatly accelerated as to indicate the splitting off of water of constitution. Above  $150^{\circ}$  the water contained considerable quantities of acetic acid, from 20% to 40% of the total condensate, and showed, in addition, traces of acetones, aldehydes, and methyl alcohol. The upper limit of temperature in their studies was  $200^{\circ}$ .

Porter and Ovitz<sup>1</sup> made an extended study of the volatile matter of coal with a view to determining the influence of the gas composition factor on the efficiency in the use of coal in various industrial processes with special reference to gas producer, coke oven and gas retort operation.

Their investigations show that the composition of the volatile matter of a coal depends largely upon the character of the coal itself. The gases from the younger coals of the West compared with those from the coals of the Appalachian region have high percentages of carbon dioxide and carbon monoxide. Because of the readiness with which these gases are given off even at comparatively low temperatures ( $300^{\circ}$ - $500^{\circ}$ ), the writers conclude that these western coals contain compounds having a direct carbon linkage such as the complex alcohols, aldehydes and acids. They show, further, that contrary to the theory of Dulong, who assumed that in combustion all the oxygen of a coal combined with hydrogen, in the case of certain low grade highly oxygenated coals nearly two-thirds of the oxygen appears in the volatile products in union with carbon, and that this fact accounts for the discrepancy between the determined heat value and that calculated by Dulong's method.

Higher hydrocarbons such as ethane are produced in greatest abundance from the eastern coals and they, consequently, yield more smoke in combustion. In general, however, the gas evolved from any coal subjected to moderate heat only, is rich in the higher paraffins such as ethane and propane. In the case of Connellsville coal, at furnace temperatures of  $500^{\circ}$  and  $600^{\circ}$  these higher hydrocarbons constitute about 50% of the total paraffin content. At about  $800^{\circ}$  the percentage reaches a maximum, when it rapidly falls on account of decomposition by heat.

They conclude that the nature of the volatile products distilled from coal in the early stages of heating varies in accordance with the smoke producing tendencies of that coal. They

<sup>1</sup>The Volatile Matter of Coal. Bull. 1. Bureau of Mines. 1910.

include among the smoke-producing constituents, tar, benzene, ethylene, and the higher homologues of methane.

E. Boernstein<sup>1</sup>, subjecting eight Westphalian coals to a maximum temperature of 450°, reports that the gaseous products of distillation did not exhibit differences corresponding with those shown by the coals themselves. Compared with ordinary coal gas, they were characterized by a higher content of heavy hydrocarbons (5% to 14%) and of methane and its homologues (55% to 76%), and a lower content of hydrogen (5% to 16%). The tars had a specific gravity between .95 and .98, began to distill at about 70° to 80°, and were found to contain no aniline, thiophene, naphthalene, or anthracene. He states that the solid paraffin content ranged from .3% to 2% (m. pt. 55° to 60°).

Inasmuch as in modern gas retort operation portions of the coal do not reach their maximum temperature for one or two hours, the subject of low temperature distillation is of real importance to the gas industry. In a paper read before the Michigan Gas Association, White, Park and Dunkley<sup>2</sup>, report the results of their studies of the primary reactions involved in heating American coals to 500°.

Gas evolution commences only above 300° and that given off in the 300° to 350° interval contains from 25% to 40% of ethane. Above the latter point the yield of ethane diminishes and very little is produced between 450° to 500°. The illuminants decrease with increasing temperature starting with 8% at 300° and going down to zero at 500°. Methane starting with small amounts reaches its maximum in the 400° to 450° interval. They call attention to the similarity of the gases produced at low temperature to natural gas and suggest that the latter was also produced at low temperature. They give the following results of analyses:

TABLE 13  
AVERAGE YIELD AND COMPOSITION OF GAS FROM COAL HEATED FOR SIX TO EIGHT HOURS AT TEMPERATURES OF 300°-500°

| Coal<br>Volume in cu. ft. per lb. of | Pittsburgh,<br>Penna. | Bay City,<br>Mich. | Zeigler<br>Ill. |
|--------------------------------------|-----------------------|--------------------|-----------------|
| Coal.....                            | 1.42                  | 1.15               | 0.63            |
| CO <sub>2</sub> .....                | 2.9                   | 16.2               | 13.1            |
| Illum.....                           | 2.2                   | 4.1                | 1.6             |
| CO.....                              | 6.2                   | 5.0                | 5.8             |
| H <sub>2</sub> .....                 | 26.3                  | 16.4               | 13.9            |
| CH <sub>4</sub> .....                | 47.0                  | 37.8               | 38.0            |
| C <sub>2</sub> H.....                | 13.2                  | 11.8               | 19.5            |
| N <sub>2</sub> .....                 | 2.7                   | 9.1                | 7.8             |
| Calculated B. t. u.....              | 902                   | 778                | 871             |

<sup>1</sup>Jour. Soc. Chem. Ind. 25-213. (1906).

<sup>2</sup>Am. Gas Light Jour. 89-621. (1906).



The apparent similarity between the gases evolved from coal at low temperatures and natural gas, gives interest to the work of Cady and McFarland<sup>1</sup> on the composition of the natural gases of Kansas. They proved the presence of paraffins heavier than methane and ethane, by condensing higher boiling hydrocarbons along with the methane in a bulb surrounded with liquid air. Some of these remained liquid up to ordinary temperatures and had an odor similar to that of light boiling petroleum distillates. The quantity of this residue varied in the different gases.

Professor V. B. Lewes<sup>2</sup> in discussing the relative merits of high and low temperatures for gas distillation, gives parallel tables showing the net cost of 1000 cu. ft. of gas produced by each of the two processes.

TABLE 14  
COST OF 1000 CU. FT. OF GAS

| (1) High (900°)         |              | (2) Low (400°) |              |
|-------------------------|--------------|----------------|--------------|
|                         | pence        |                | pence        |
| Coal.....               | 13.30        |                | 26.50        |
| Operating expenses..... | 6.74         |                | 5.50         |
|                         | <u>20.04</u> |                | <u>32.00</u> |

LESS VALUE OF RESIDUALS PRODUCED

|                               |          |             |          |              |
|-------------------------------|----------|-------------|----------|--------------|
| Coke.....                     | .82 cwt. | 6.11        | 2.4 cwt. | 17.64        |
| Tar.....                      | .9 gal.  | 1.30        | 4.6 gal. | 6.90         |
| NH <sub>4</sub> products..... |          | 2.11        |          | 2.80         |
|                               |          | <u>9.52</u> |          | <u>27.34</u> |

NET COST OF GAS

|                          |      |
|--------------------------|------|
| 10.52.....               | 4.66 |
| B. t. u. of gas 592..... | 750. |

He points out that although the coke residues are figured at the same price, coke (2) is really more valuable since it contains 15% of volatile matter which increases its calorific value. He states also that the low temperature tar distillates contain valuable fractions of a character different from those obtained from ordinary gas tar, one of which is especially suitable for use in motors as a fuel.

Burgess and Wheeler<sup>3</sup> working on the problem of the prevention of mine dust explosions, and recognizing the relationship

<sup>1</sup>Jour. of Am. Chem. Soc. 29, 1523. (1907).

<sup>2</sup>Engineering. 85-410. (1908).

<sup>3</sup>Jour. Chem. Soc. 97-1917. (1910).

that exists between the character of the volatile matter escaping from a heated coal, and its degree of inflammability, studied the composition of the gases evolved at different temperatures.

They found that with all coals whether bituminous, semi-bituminous, or anthracite, there was a well-defined decomposition point at a temperature between 700° and 800° which corresponds to a marked increase in the quantity of hydrogen evolved. This increase they attribute to the thermal decomposition of one or more of the higher homologues of methane yielding hydrogen and carbon. Ethane, propane, butane, and, probably, higher members of the paraffin series, form a large percentage of the gases given off at temperatures below 450°; above 700° they no longer appear.

They believe that the smoke producing elements consist almost entirely of the higher paraffins and differ from Porter and Ovitz in excluding ethylene and the related unsaturated gases from this class. This view is based upon experiments made showing that ethylene decomposing at 600°, deposited very little carbon.

A typical analysis of the gases obtained is given below.

TABLE 15  
GAS FROM COAL FROM ABERTILLERY, SOUTH WALES (BITUMINOUS)

| Coal (C) | Temp. | Illum. | CO <sub>2</sub> | CO   | H <sub>2</sub> | CH <sub>4</sub> | C <sub>2</sub> H <sub>6</sub> |
|----------|-------|--------|-----------------|------|----------------|-----------------|-------------------------------|
|          | 500°  | 5.8    | 3.9             | 4.7  | 8.0            | 64.5            | 11.0                          |
|          | 600°  | 4.9    | 3.2             | 6.4  | 25.0           | 47.2            | 12.4                          |
|          | 700°  | 2.8    | 3.4             | 7.4  | 34.7           | 46.2            | 4.2                           |
|          | 800°  | 2.8    | 2.5             | 9.8  | 50.8           | 28.6            | 4.7                           |
|          | 1100° | 4.2    | 1.4             | 13.0 | 60.7           | 18.8            | 1.8                           |

In a second paper<sup>2</sup> they discuss the results obtained by subjecting coals to a series of fractional distillations in a vacuum and determining the compositions of the gases evolved within well defined limits of temperature. They succeeded by prolonged exhaustion at a low temperature, in removing entirely the paraffin-yielding constituents and leaving behind a compound which decomposed at a comparatively high temperature, yielding only hydrogen. They conclude, therefore, that coal is composed largely of two types of compounds, the one unstable, giving no hydrogen, the other more stable yielding hydrogen only.

<sup>1</sup>Jour. Soc. Chem. Ind. 5, 2. (1886).

<sup>2</sup>Jour. Chem. Soc. April, 1911, p. 649.

G. E. Davis<sup>1</sup>, discussing the tars formed under different conditions, says that at low temperatures are produced mainly such hydrocarbons as belong to the paraffin series having the general formula  $C_n H_{2n+2}$ , along with the olefines  $C_n H_{2n}$ . The lower members of these series are liquid, and, furnished in the pure state, are illuminating and lubricating oils; the higher ones are solid and form commercial paraffin. They are always accompanied by phenols. Liquid products prevail and among the watery substances acetic acid predominates.

If, on the other hand, the coal has been decomposed at a very high temperature, the molecules are grouped quite differently. While olefines and acetylenes occur more or less the paraffins disappear almost entirely with the resultant deposition of carbon.

Some of this carbon set free is deposited in the retort in a compact graphitoidal form; some occurs in a state of extremely fine division in the tar and forms a constituent of the pitch or coke remaining behind. At the same time the action of heat effects molecular condensations by which process compounds of a higher molecular weight are formed, such as naphthalene, anthracene and phenanthrene.

Behrens<sup>2</sup> found that the tar obtained in the distillation of coal in the ordinary fire-clay gas-retorts (operated at high temperatures) was much richer in benzene, toluene, naphthalene, etc., than the tar made in Pauwel's coke ovens (operated at low temperatures) from the same kind of coal.

Lunge<sup>3</sup> thinks that at low temperatures most of the nitrogen of the tar is in the form of aniline and fatty amines (ethylamine, propylamine, amylamine); at high temperatures in the form of pyridine bases, picoline, lutidine, viridine, etc. He admits that the statement needs verification by more detailed investigations. In general, at high temperatures the tendency to complete dissociation becomes far more pronounced: the products approach more and more to free carbon on the one hand and free hydrogen on the other.

Watson Smith<sup>4</sup> states that naphthalene increases with rise of temperature. This is true also of anthracene, which is then found in the creosote oil coming over before the anthracene oil proper. Carbolic acid is also an important constituent.

<sup>1</sup>Jour. Soc. Chem. Ind. 5, 2. (1886).

<sup>2</sup>Dingler's Polyt. Journal 208, 362.

<sup>3</sup>Coal Tar and Ammonia, p. 26. (1900).

<sup>4</sup>Jour. Soc. Chem. Ind. 8, 950. (1890).



## II. STUDIES IN GENERAL ON THE CARBONIZATION OF COAL

F. C. Keighley<sup>1</sup> argues that since the chemical constituents of coals from any horizon are not necessarily indicative of their coking properties, it is reasonable to assume that an important factor determining the coking quality must be one of a physical character and not altogether chemical.

It is known, he says, that the finest coking coals not only are of the bituminous class, but their structure is such that upon fracture they exhibit a fingery or prismatic form and separate vertically, while the more difficult coking coals and the ones of a bituminous character that cannot be coked at all, are of a laminated structure and upon fracture break into cubical form and have a tendency to separate horizontally instead of vertically. This he thinks would indicate that the coking property depends very largely upon the arrangement of the small particles of coal composing the seam. If these lie in the seam with their longer axes horizontal to the bedding of the seam they are unfavorable to the coking process. On the other hand, if they are perpendicular to the strike of the seam, i.e., at right angles with its bedding, the coking tendency is much more pronounced. He suggests that the superiority of Connellsville coke may be due to the structure given it in the process of formation by the peculiar geological movements of the region in which it is found.

M. A. Pishel<sup>2</sup> suggests a simple practical test for coking coal. Pulverize the coal to 100 mesh in an agate mortar. Pour out the dust and observe its condition. If it adheres strongly to the mortar, it will probably make good coke, he says. If there is little adhesion, coking properties are absent. In his experimental work he tested more than 150 different specimens. Of the four Illinois coals tried, none stuck to the mortar while most of the Eastern coals adhered. He offers no theory to account for this phenomenon.

Groves and Thorp<sup>3</sup> classify coals with respect to their coking properties as sand coals, those devoid of coking powers; sinter coals, those possessing it to a relatively slight degree; coking coals, those which produce a good quality of coke, and anthracite.

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<sup>1</sup>Iron Age. 80-364. Aug. 1907. Mines and Minerals Oct. 1907.

<sup>2</sup>Econ. Geol. June-July 1908. p. 265-270.

<sup>3</sup>Chem. Tech. Vol. 1, p. 122 (ed. 1889)

They give the following analytical table made up from the work of Richardson, Regnault and others:

TABLE 16

|                  | (Percentage) |   |    |
|------------------|--------------|---|----|
|                  | C            | H | O  |
| Sand coal.....   | 77           | 5 | 18 |
| Sinter coal..... | 83           | 5 | 12 |
| Coking coal..... | 87           | 5 | 8  |
| Anthracite.....  | 95           | 3 | 2  |

TABLE 17

|                                |                 |
|--------------------------------|-----------------|
| Anthracite.....                | 80C + 88H + 0   |
| Blanzy sinter.....             | 80C + 123H + 60 |
| Lancashire cannel sinter.....  | 80C + 128H + 30 |
| Mons coking.....               | 80C + 24CH + 50 |
| Grand Croix-highly coking..... | 80C + 112H + 30 |

It will be observed from Table 16 that the amount of hydrogen in the first three varieties is identical, while the oxygen diminishes as the coking property is developed. The Grand Croix coal (Table 17) has only half the amount of hydrogen contained in the coking coal from Mons. Anthracite, consisting almost entirely of carbon, may be considered a kind of natural coke.

They state in conclusion, however, that Stein of Dresden has shown that coking and non-coking coals may have the same ultimate composition and that simple analyses, therefore, cannot determine absolutely the coking property of the coal. They suggest that the real source of coking lies in a resinoid body or bodies identical in composition with the coke itself.

White and others<sup>1</sup> mention the work of Ste. Clare Deville, consulting chemist of the Paris Gas Company, who, on the basis of results of nearly 2000 tests, divided coals into groups according to the relations of their percentages of oxygen to hydrogen. He found that all coking coals contain a percentage of oxygen approximately twice that of hydrogen.

They reasoned that possibly the artificial application of heat which gives as its first products water and other compounds rich in oxygen, would lower the relatively high oxygen of the non-coking coals and possibly bring them into the coking class. They found, however, that coals which were originally non-coking were not improved in this respect even though the oxygen-

<sup>1</sup>Am. Gas Light Jour. 89-621. (1906)

hydrogen ratio was brought down to 2 to 1. The coking coals tested sintered together during the heating and if the resultant mass was heated to redness it retained its shape and gave a good coke. If, however, it was powdered before being heated, it remained a powder.

Dr. Haberman<sup>1</sup>, in studying the spontaneous heating of coals, noted the fact that long storage tends to destroy both gasifying and coking properties. He found that those coals that oxidized the most and gave the greatest rise in temperature absorbed the largest quantities of bromine.

Professor Fischer<sup>2</sup> of Göttingen, working on the same problem, mentions the loss of coking suffered by oxidized coals. He too suggests the bromine absorption test for determining the chemical activity of the fuel.

Parr and Lindgren<sup>3</sup> doing work on the weathering of coal at the University of Illinois observed that in volatile matter determinations, samples exposed for several months gave powdery residues instead of coke as in the case when fresh coals were used.

David White<sup>4</sup>, in his bulletin "The Effect of Oxygen in Coal," after discussing the negative calorific value of the oxygen and the transition between various grades of coal due to progressive devolatilization brought about more or less directly by dynamic forces, takes up a study of the relative proportion of oxygen, hydrogen, and carbon, in coking coals with special reference to a theory framed to explain the coking quality.

He mentions the work of Regnault<sup>5</sup> and Bertrand,<sup>6</sup> who found that the high percentage of volatile matter and the high illuminating value of certain bogheads and oil shales are due to the presence of immense numbers of supposed gelatinous algæ which, in these coals, seem to have exercised a selective attraction for certain bituminous compounds. Likewise, the conditions of accumulation and deposition attending the origin of many coals were doubtless favorable for the mingling of algæ and different animal remains with the debris of higher plant types.

Mr. White thinks it is more than probable that the substances of these lower organisms contributed as ingredients to

<sup>1</sup>Schillings Jour. fur Gasbel. 49-419, (1906)

<sup>2</sup>The Gas World. April 13, 1901.

<sup>3</sup>Unpublished reports of supplementary studies to Bulletin No. 17, University of Illinois. Engineering Experiment Station. (1911)

<sup>4</sup>Bull. U. S. G. S. 382 (1909)

<sup>5</sup>Regnault, B. Les micro organismes des combustibles fossiles. St. Etienne, 1903.

<sup>6</sup>Bull. Soc. d'hist. Nat. Antun. Vol. 9, 1897, p. 193.



the mass of coal-forming material, and that they, therefore, exerted some influence on the character and quality of the final residues. He considers the higher percentage of bituminous matter in the older and more altered condition of the fuel, due to concentration as the result of devolatilization of the coal by dynamochemical processes, the larger part of the concentration being the result of loss of oxygen, this loss being disproportionately great as compared with that of hydrogen. Thus, the progressive deoxygenation of the organic matter accomplishes bituminization.

Now, he continues, the qualities of fusibility and swelling concurrent with bituminization which appear to characterize fuels known to contain quantities of gelatinous micro-algæ, are also necessary to the coking quality in coals, and he thinks it permissible, therefore, to inquire whether the coking property may not be due to some unascertained proportion of gelatinous algal matter entering into the original mass from which the coal was formed and imparting to it this fusibility and tendency to swell.

While the presence of micro-algal ingredients has been noted in peats and even in some brown coals, yet it is very evident that their detection by microscopical means in the highly metamorphosed coking coals, is so difficult as to be practically impossible. The evidence of chemical analysis must therefore, be called into service. The coals, he says, whose large volatile combustible matter contains relatively the highest hydrogen and the lowest oxygen, thus approaching nearest the bitumen analyses, are those in which the organic remains described as micro-algæ are most predominant and best preserved. If then, in the high volatile coals high bituminization and gelatinous algal ingredients go together and the presence of the latter causes the coal to fuse and swell, we may conclude that high volatile coals that show sufficiently high bituminization will coke by the ordinary process. The degree of bituminization is indicated by the relative excess of hydrogen as compared with the diminished oxygen in dry coal and is expressed by the ratio H:O.

Data covering the tests of over 300 coals from different localities furnished by the U. S. Geological Survey are given. It was found that those coals having a H:O ratio of 59 or more, coke by the ordinary commercial process. Nearly all below 59 and above 55 so far as tested, make a coke. Those below 55 us-

ually give a poor and dark product. The best cokes obtained by the ordinary process were made from coals having a ratio of 60 or over. It was noted however that with coals with a fixed carbon value of over 79 per cent the rule breaks down.

He remarks that his hypothesis appears to harmonize with the tendency of coking coals to cohere when reduced to fine powder, discussed by M. A. Pishel.

O. Boudouard<sup>1</sup> took up the study of coals with the specific purpose of determining the causes of coking and selected for experiments samples of (1) English anthracite, (2) Courrieres ( $\frac{1}{4}$  bituminous), (3) Belgian forge coal, (4) Forge coal of unknown origin which has lain in the laboratory several years, (5) Bruay ( $\frac{3}{4}$  bituminous), (6) Coal of unknown origin, (7) Lignite.

The following table gives the results of the approximate analyses:

TABLE 18  
COMPOSITION OF COALS BEFORE TREATMENT

|                             | 1       | 2       | 3    | 4    | 5    | 6              | 7       |
|-----------------------------|---------|---------|------|------|------|----------------|---------|
| Fixed carbon.....           | 88.6    | 89.5    | 70.5 | 79.1 | 39.3 | 51.4           | 37.3    |
| Ash.....                    | 2.5     | 1.6     | 4.6  | 2.6  | 3.1  | 2.3            | 4.2     |
| Volatile matter.....        | 8.8     | 8.8     | 24.8 | 18.1 | 37.6 | 46.2           | 58.4    |
| Character of coke.....      | powdery | powdery | hard | hard | hard | slightly caked | powdery |
| Hardness <sup>2</sup> ..... | 0       | 0       | 3    | 3    | 3    | 0              | 0       |

These coals were successively subjected for periods of 105 hr. each to the action of air at 15° and 100°. After the first treatment little change in the coal and in the appearance and character of the coke was noted except that No. 6 and 7 showed traces of humic acid. In contrast with this, after being heated at 100°, none had retained their coking powers and all but (1) and (2) contained humic acid. A marked increase in weight due to oxygen absorption was observed, amounting in some cases to nearly 5 per cent.

He further treated 25 grams of each of the coals studied with 150 grams of concentrated nitric acid for a period of 2½ months. Analyses of the residues gave the following results:

<sup>1</sup>Bull de Ca. Sec. Chim. 5 (series 4) 365-39 (1909).

<sup>2</sup>The relative hardness of the coke is indicated by the figures 3, 2, 1, 0, -3 denoting a hard compact coke, 0, a powdery residue.

TABLE 19  
COMPOSITION OF COALS AFTER TREATMENT WITH NITRIC ACID

|                                 | 1        | 2        | 3           | 4          | 5                          | 6                          | 7           |
|---------------------------------|----------|----------|-------------|------------|----------------------------|----------------------------|-------------|
| Per cent change in weight . . . | + 15.6   | + 26.0   | + 6.4       | + 20.4     | + 17.2                     | — 14.0                     | — 36.8      |
| Fixed carbon . . .              | 68.1     | 54.7     | 56.5        | 51.5       | 49.6                       | 43.2                       | 39.4        |
| Ash . . . . .                   | 1.8      | .41      | 1.5         | 6.1        | 1.6                        | .72                        | .61         |
| Vol. matter . .                 | 30.1     | 44.8     | 41.9        | 42.2       | 48.7                       | 56.0                       | 59.9        |
| Appearance of coke . . . .      | powdered | powdered | powdered    | powdered   | traces of agglome-<br>rate | traces of agglome-<br>rate | powdered    |
| Humic Acid . .                  | 0        | 0        | 15 per cent | 8 per cent | 50 per cent                | 40 per cent                | 27 per cent |

Organic solvents such as ligroin, pyridine, benzene, carbon disulphide, carbon tetrachloride and the like, modified in no appreciable way the quality of the coke produced. Concentrated sulphuric acid destroyed the coking power; concentrated hydrochloric acid had no effect.

In none of these coals did humic acid exist before treatment and since its presence was always constant in the same oxidized coals which had in the process lost their coking powers, working on the theory that the carbohydrates were responsible for the origin of the acid, he found that starch or sugar treated with bromine water, for instance, yielded humic acid much like that obtained from coal.

It is probable, he thinks, that the hydrocarbonaceous substances giving rise to this acid do not exist in a single form but in a state of great condensation, and polymerization is a result of the decomposition of the living matter, the principal characteristics of this series of processes being the disintegration of the plant tissues and the accumulation of carbon at the expense of hydrogen and oxygen.

In his comparative studies of natural and oxidized coals, he noted that the production of a very small quantity of humic acid (less than 1 per cent) marked the disappearance of the coking qualities of the original sample.

In this connection the theories advanced by Professor Lewes, already referred to, on page 25, are of interest, harmonizing as they do with Boudouard's work and presenting some of the most modern lines of thought on this subject.

Dennstedt and Bunz<sup>1</sup> hold with Boudouard that humic acids

<sup>1</sup>Zeitsch. f. ang. Chem. 21, 1825. (1908).



are the ultimate oxidation products of coals and the most inflammable coals are those that produce the largest quantities of the acid.

The exact nature and composition of the so-called humic acids, however, seem to be unknown. Boudouard<sup>1</sup> quotes the results of several experimenters who produced the substance by treating sugar with acids. The empirical formulas (no structural formulas are attempted,) range from  $C_{24}H_{18}O_9$  (Stein) to  $C_{40}H_{24}O_{12}$  (Mulder). He himself proposes  $C_{18}H_{14}O_9$  as the composition of humic products he obtained by extracting oxidized coal with potassium hydroxide.

W. C. Anderson in studying the varying coking tendencies of a number of Scotch coals, concluded that cementation is caused by the decomposition of two classes of substances; (1) resinous materials soluble in caustic potash, which break down on rapid ignition; and (2) non-saponifiable substances, some of which were volatile at  $300^\circ$ , others being stable at this temperature.

### III. SUMMARY OF OPINIONS

A very brief review of the literature covering the decomposition that takes place at low temperatures in the distillation of coal, is sufficient to prove to the student that the problem in all its phases is distinctly modern. A glance at the bibliography will show that few, if any, references date back more than ten years and that most of the publications on the subject have appeared within the last two or three. Indeed, Burgess and Wheeler<sup>2</sup> writing in 1910, remark that "previous work has been very scanty". Furthermore, almost without exception, those investigators who have already made reports announce that their first articles are more or less incomplete and that they expect to continue along the same lines of study.

While the development of the subject is evidently still in its infancy, yet results from different sources are in many cases entirely consistent. Of particular interest in that it bears a close relationship to the problem of smoke prevention, is the fact, mentioned by nearly all authorities, that the heavy smoke-producing benzines and paraffins of high carbon content are given off at

<sup>1</sup>Bull. de la Soc. Chim. 5 (series 4) 378. (1909).  
Jour. Soc. Chem. Ind., 17-1013. Nov., 1898.

<sup>2</sup>Jour. Chem. Soc. 97-1917 (1910)

low temperatures and are practically eliminated at  $500^{\circ}$ . Attempts to separate and estimate the higher homologues of methane contained in early distillates, however, have not been entirely successful on account of a lack of adequate methods of gas analysis. Cady and McFarland<sup>1</sup>, using liquid air, got perhaps the best results but even their scheme leaves much to be desired. Writers reporting the paraffin content of the gases studied therefore have been obliged to estimate the heavier members as "ethane", or, using the formula  $C_n H_{2n+2}$ , to give average values of  $n$ .

It is generally agreed further, that as temperatures rise above  $500^{\circ}$ , methane and hydrogen are the principal gas constituents, being decomposition products of not only the coal itself but of some of the gases given off at the lower temperatures. Below  $400^{\circ}$ , hydrogen is present in very small amounts. It seems fairly well established, therefore, that the density and, consequently, the calorific value of a gas varies inversely with the temperature at which it is evolved and that a very moderate heating of the coal is sufficient to remove enough of the smoke producing elements to make the combustion of the residue clean and economical.

With a very small amount of work done in determining the character of the low temperature tar distillates, a fruitful field is left for future investigation. Paraffin oils, valuable for lubricating and power generating, seem to predominate, while the equally important aromatic derivatives, as anthracene, are present to a less extent than in the high temperature runs.

The investigations of Parr and Francis prove that coal, modified by the application of moderate heat gains valuable properties and that it retains a high calorific value. In the use of certain types of coal, however, such as those of the central west, the problem of putting the residues into marketable condition demands a solution before the process can be made an economic success.

Much has been written in attempts to explain the causes of coking, or at least to define the conditions that govern it. From the work of Parr, Chamberlain, Boudouard, and others, who have studied the reactions taking place at low temperatures, it has been proved that oxygen absorption goes on rapidly when fresh coal is exposed to the atmosphere. It has been shown

<sup>1</sup>Jour. Am. Chem. Soc. 29—1523 (1907)

further that this absorption weakens or destroys altogether any coking properties that the original coal may have. In other words a high oxygen-hydrogen ratio marks the absence of fusibility and cementation.

The structures of the organic compounds of the coal which furnish the cementing material for coke and which are apparently attacked by oxygen, have not been determined and seem to vary somewhat in different types of coals. However they yield, on oxidation, humic acids of varying composition which decompose into powdery residues. Because of the complex nature of these substances and the difficulty experienced in isolating and identifying them, the matter of coking is still an open problem and the explanations advanced are largely hypothetical.



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